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Thermoelectric Battery Based on Bundles of Bi and Sb Nanowires in Anodic Alumina Matrices

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Abstract—A model of a microthermoelectric battery consisting of series connected thermoelectric cells of one-dimensional nanostructures formed into bundles by external contacts is proposed. The electrochemical processes of forming Bi and Sb nanowire arrays with the required dimensions and physicochemical properties in porous anodic alumina templates with large length-to-diameter ratios are studied and developed. The design and basis of the fabrication technology of microthermoelectric battery branches are developed, whose heat flow density will be controlled by the Seebeck coefficient measured at external contacts connecting the nanowire ends. It is shown that a set of parallel branches in the battery can be fabricated due to a high density of nanowire packing in a porous matrix, which will make it possible to achieve a fundamentally higher increase in the microheat meter efficiency.

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The development of highly sensitive devices for measuring heat flux densities is essentially important for saving heat power resources in industry, power engineering, and transport. The thermoelectric effect is excellently suited to measuring the heat flux using a thermoelectric battery consisting of series connected branches of different thermoelectric materials, by the auxiliary wall method, by measuring the temperature difference between isothermal planes of a thin plate with known thermal conductivity [1]. The density of the heat flux permeating such a battery will be determined by the Seebeck coefficient in it. The sensitivity, speed, operating temperature range, the degree of matching of the thermoelectric heat meter with a medium are first of all controlled by the used thermoelectric materials [2]; however, their efficiency increases many times when using nanostructured thermoelectric materials [3]. Among the physicochemical methods for producing nanostructures and nanowires of metals and semiconductors, the most attractive method is the electrochemical deposition of these materials into specially prepared templates of nanoporous anodic aluminum oxide (AAO) [4, 5].

In the present study, we propose the model of a thermoelectric cell based on nanowire arrays combined into a bundle by external contacts (Fig. 1a) and the technology for fabricating thermoelectric batteries based on bismuth and antimony nanowires with large length-to-diameter ratios. Calorimeter battery branches consisting of thermoelectric cells connected in series (Fig. 1b) will represent isothermal planes in the path of the measured heat flux, and the Seebeck coefficient measured at the nanowire ends will define the heat flux density [6]. Due to the high packing density of nanowires in AAO, many parallel branches can be formed in the battery of thermoelectric cells, which will make it possible to increase the heat-meter efficiency [7].

To implement the proposed thermoelectric battery, a technological route was developed and the formation of AAO matrices and the deposition of Bi and Sb nanowire arrays in them were worked out. Figure 2 shows the sequence of technological operations of this route. The AAO matrices for depositing nanowires are fabricated by the two-stage double-sided electrochemical anodization of Al (99.99%) foil (Figs. 2a and 2b) in a 0.2-M solution of oxalic acid under conditions providing the required porous AAO nanostructure [8]. After formation of an AAO layer of required thickness, a copper layer was deposited in vacuum onto the porous AAO surface (Fig. 2c). Then, AAO and the remaining aluminum layer were sequentially selectively removed from the opposite side (Fig. 2d). After photolithography (Fig. 2e), to produce a bismuth nanowire array, the barrier oxide layer was removed through windows in the photoresist (Fig. 2f). Pore cleaning and expansion were performed through

† Deceased.

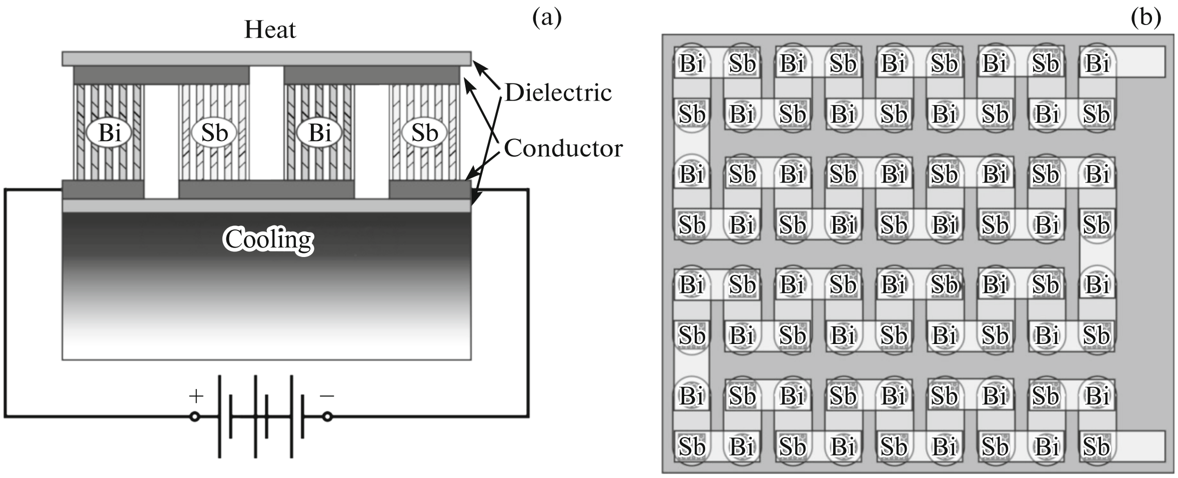

Fig. 1. (a) Schematic diagram of a thermoelectric cell based on arrays of Bi and Sb nanowires and (b) the thermoelectric battery of thermoelectric cells connected in series.

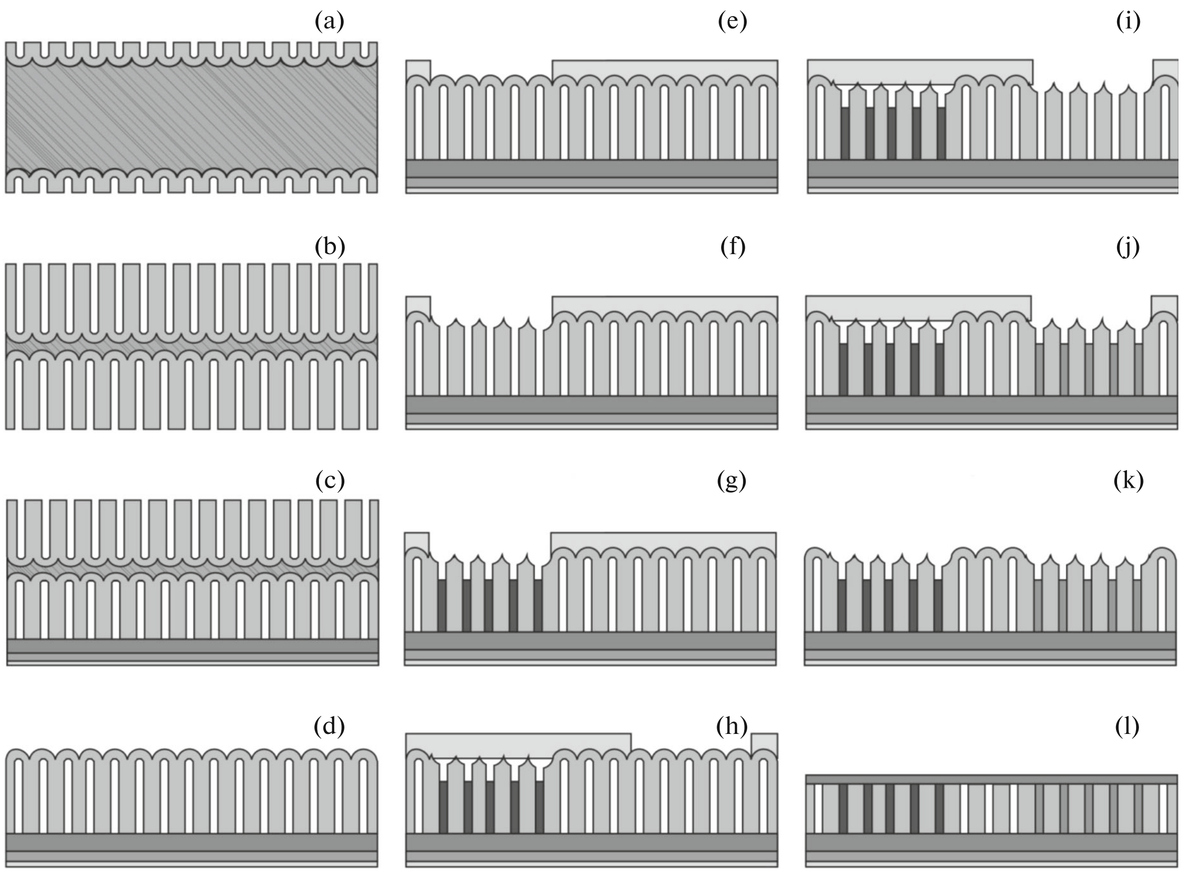

Fig. 2. Sequence of technological operations of producing a thermoelectric cell based on Bi and Sb nanowire arrays in an AAO matrix.

open pores; copper films 2–3 μm thick were additionally electrochemically deposited onto cleaned copper areas near the pore bases. The technological process is described in more detail in [8].

The electrochemical deposition of bismuth into windows of the prepared AAO matrices was performed from a 0.13-M $BiCl_3$ + 1.2-M NaCl + 1-M HCl solution into pores on a copper sublayer counteretched in

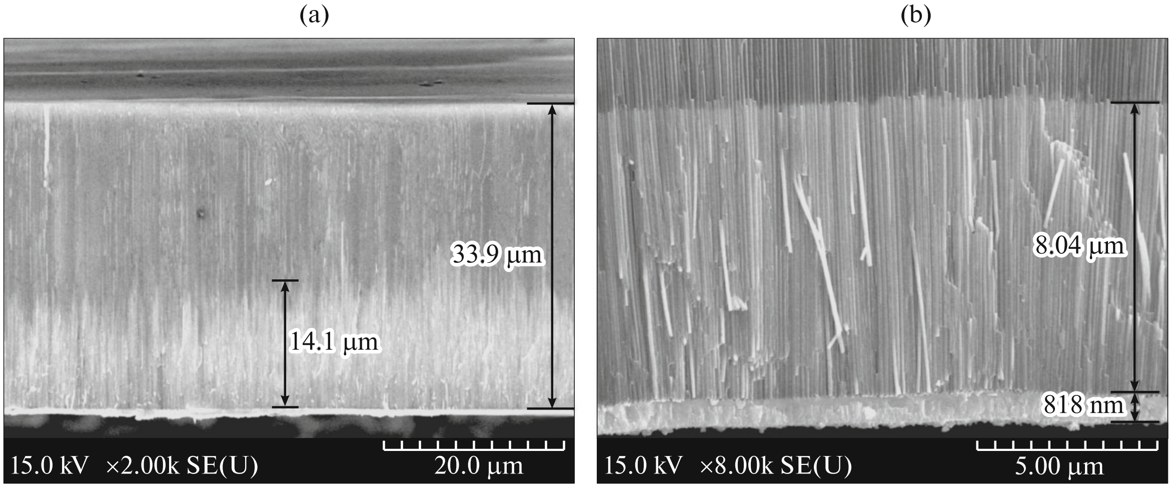

Fig. 3. Cross sections of AAO matrices with (a) Bi and (b) Sb nanowires.

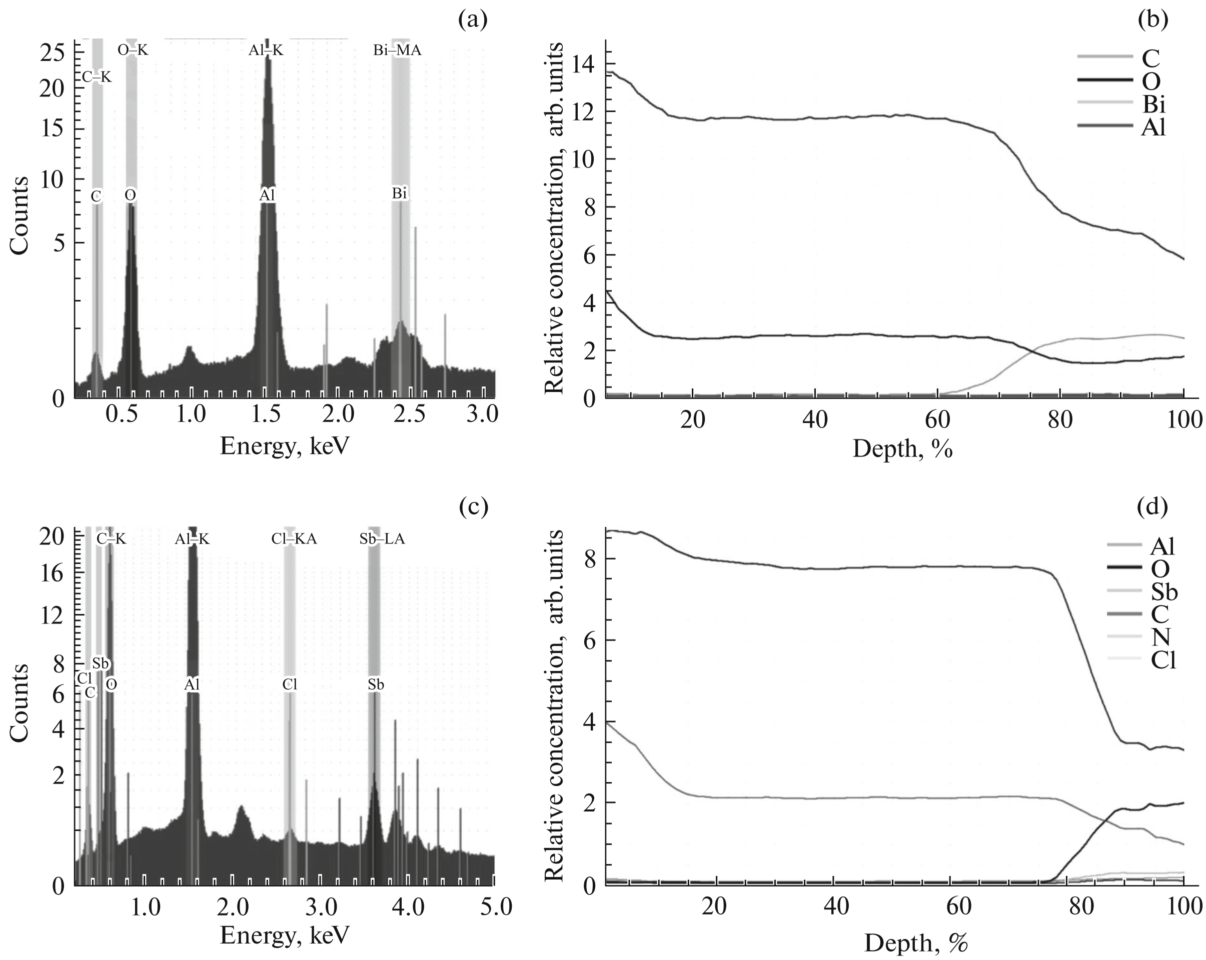

Fig. 4. Spectra of the electron probe X-ray microanalysis of (a) Bi and (c) Sb and distribution profiles of elements in the AAO matrix with (b) Bi and (d) Sb nanowires.

a 5% sulfuric acid solution (Fig. 2g) at a cathodic current density of 19.2 mA/cm^2.

Then, after photolithography, to produce Sb nanowire bundles (Fig. 2h) and to dissolve the barrier oxide layer (Fig. 2i), antimony was deposited into prepared pores from a 0.16-M $SbCl_3$ + 0.55-M HCl solution with added EDTA (Fig. 2j) at a current density of 10.7 mA/cm^2. Under these electrochemical condi-

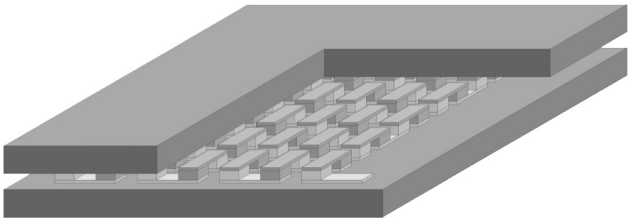

Fig. 5. Model of the thermoelectric battery of a heat meter based on Bi and Sb nanowire bundles.

tions, a high reproducibility of bismuth deposition into AAO matrix pores with a deposition rate of 0.61 μm/min and uniform antimony deposition with a rate of 0.195 μm/min was provided. The deposition time was 23.5 min for Bi and 41 min for Sb. After planarization of the AAO matrix surfaces, a copper layer was deposited in vacuum on the substrate through a mask with the result that electrical contacts to bismuth and antimony nanowire arrays were formed (Fig. 2l).

Electron microscopy studies of the formed structures performed using a Supra 55 WDS scanning electron microscope at an accelerating voltage of 15 kV showed that electrochemical deposition resulted in the formation of Bi and Sb nanowires with diameters corresponding to pore diameters of 55 nm in each pore (Fig. 3). The packing density of the nanowires was $\sim 1.45 \times 10^{10}$ units/cm^2, and the cross-sectional area of each nanowire was $\sim 1.25 \times 10^{-12}$ cm^2. The developed technology allows the formation of regular arrays of nanowires 10–100 μm long, from 30 to 70 nm in diameter, and distances between them of 40–100 nm.

Thus, by creating templates of AAO membranes with various pore sizes and varying the deposition time, nanostructures with various diameter-to-length ratios, hence, with different electrical properties can be fabricated.

Figure 4 shows the results of studies of the Bi (Fig. 4a) and Sb (Fig. 4b) nanowire composition in the porous AAO template in the form of electron probe X-ray microanalysis spectra. Both spectra contain lines corresponding to the elemental composition of the initial matrix: the line with a maximum at 1.62 eV corresponds to aluminum in the AAO membrane structure, the line with a maximum at 0.51 eV corresponds to oxygen, and the line with a maximum at 1.48 eV corresponds to partially oxidized copper in the pores. The formation of nanowires in the pores due to electrochemical deposition is reflected in the spectrum by several lines corresponding to bismuth in different forms (1.87, 2.52, 2.57, and 2.74 eV) with the maximum band at 2.42 eV and to antimony (3.2, 3.82, 4.15, and 4.6 eV) with the maximum band at 3.59 eV. Carbon with a maximum at 0.19 eV, which was incorporated into the template from the electrolyte during anodization was also detected in the composite structure. Chlorine (2.6 and 2.87 eV) was also detected in the sample, which, probably was incorporated into the composite structure from the electrolyte for antimony deposition.

Among the tested materials (bismuth and antimony), semiconductors with a high mobility and electron density are also most attractive for producing chains of nanowires. Of particular interest is the use of semiconductor–semimetal and semiconductor–conductor compositions, since the Seebeck coefficients of semiconductors are higher than those of semimetals by an order of magnitude and more.

The developed techniques allow the reproducible production of nanowires of metals, semimetals, and semiconductors with required physicochemical properties, which offers prospects for the development of a wide spectrum of thermoelectric devices and systems. In the next stage, it is necessary to create a prototype of the thermoelectric battery of a heat meter, based on the nanowire bundle schematically shown in Fig. 5, and to perform research measurements of its thermoelectric characteristics. It is planned to achieve an increase in the volt–watt sensitivity and speed of the heat meter due to the use of nanowires with a high packing density in parallel battery branches and as a result of specific quantum-size phenomena associated with additional charge carrier and phonon scattering at nanowire and external contact interfaces.

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